

Development of pH Scale-Based on the Ionic Interaction Approach (Pitzer Method)

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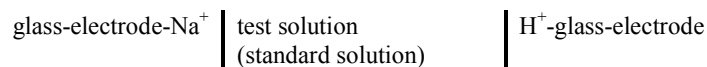
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The ionic interaction approach is suggested as the theoretical basis for the assignment of pH values for reference pH buffer solutions with variable ionic strength. Two pH scales are developed in the framework of the theoretical method. One of them is a conventional pH scale (pH_c) for pH measurements by means of cells without a liquid junction. The "True" pH scale (pH_t) is recommended to measure pH by means of cells with a liquid junction. The conventional pH_c scale is unambiguously constructed. While "true" pH_t scale demands extra thermodynamics, suggestions about some unmeasurable virial coefficients are made.

For both scales pH values are assigned to NaH_2PO_4 - Na_2HPO_4 - $NaCl$ - H_2O and TRIS-TRISHCl- $NaCl$ - H_2O buffer systems for a temperature ranges 5-40°C and 0-40°C, respectively, and a wide NaCl molality range (0-4). "True" pH_t scale turns into NBS scale at the same concentrations of buffer solutions. Good agreement between those scales is shown.

Using a conventional pH_c scale, the method of pH_c measurements of seawater by means of cell without a liquid junction has been developed. The following cell is recommended



Now, three buffer systems are available for standardization of the cell noted above: Na_2HPO_4 - NaH_2PO_4 - $NaCl$ - H_2O with $m_{HA}=m_A=0.025$ and TRIS-TRISHCl- $NaCl$ - H_2O with $m_{TRIS}=m_{TRISHCl}=0.04$ at any molality NaCl as well as TRIS-TRISHCl-seawater (TRIS-SW) with $m_{TRIS}=m_{TRISHCl}=0.04$. Good agreement was shown between the three investigated buffer systems. Since dissociation constants of carbonic acid are not available in the pH_c -scale, the conversion of pH_c values into the concentration "Total" scale (pH_T) is offered by means of a strict thermodynamic approach, using accurate EMF data of a cell constructed from Pt/ H_2 and AgCl,Ag electrodes (Dickson A.G. J.Chem. Thermodyn., 1990, V.22, p.113-127). pH_T data obtained by means of cell without a liquid junction and spectrophotometric method for the Japan Sea cruise on the R/V Prof.Khromov are compared and discussed.